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Sensitive absorption techniques for spectroscopy

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Direct absorption spectroscopy is a simple, noninvasive, in situ technique for obtaining information about gas phase species. From an absorption spectrum, quantitative absolute concentrations and absolute frequency-dependent cross sections can be extracted. However, direct absorption spectroscopy suffers from a low sensitivity that limits its extension into several research fields (e.g., trace gas analysis). This low sensitivity results from the fact that a small light attenuation has to be measured on top of a large

In 1988, O'Keefe and Deacon¹ developed a pulsed absorption technique: pulsed cavity ring down (CRD) spectroscopy. The technique is based on the measurement of the decay rate of light confined in a high-finesse optical cavity and, therefore, is insensitive to intensity fluctuations of the light source. The light enclosed inside the high-Q cavity retraces the same optical path many times (multipassing), and effective absorption pathlengths of over 1 km are easily obtained. During the last decade, CRD spectroscopy has

thermore, the experimental setup is rather simple. Additionally, the technique is applicable in all wavelength regions where components are available and thus is capable of probing a wide range of species.

Principle

A schematic representation of the experimental setup is depicted in *Figure 1*. Light from a pulsed laser is coupled into a stable, high-finesse, nonconfocal, optical cavity formed by two highly reflective mirrors (reflectivity $R > 99.5\%$) separated by a distance, d . The light inside the cavity is reflected many times back and forth between the mirrors, and at each pass, a small fraction of the light exits the cavity due to the (finite) mirror transmittance. It can easily be shown that the light intensity inside the cavity will decay exponentially. This decay is monitored by placing a detector directly behind the cavity end mirror. The time in which the light intensity inside the cavity decreases to $1/e$

CRD spectroscopy has proven to be a versatile and highly sensitive absorption technique.

background signal that in turn is proportional to the intensity of the light source. As a result, pulsed lasers, which cover a broad wavelength region (from the UV to the IR), but exhibit large pulse-to-pulse intensity fluctuations, are not well suited for these studies.

Several experimental schemes can improve the sensitivity, increasing the absorption pathlength (multipassing, for example, in a White cell or a Herriott cell), and/or combining direct absorption spectroscopy with a modulation technique (e.g., amplitude modulation, 1-f or 2-f frequency modulation). Obviously, the initial simplicity of the experimental scheme involved in direct absorption spectroscopy is abandoned when using these sensitivity-enhancing schemes. Furthermore, combining direct absorption spectroscopy with a modulation technique no longer provides direct quantitative information on an absolute scale.

proven to be a versatile and highly sensitive (detection limits typically 10^{-8} cm^{-1}) absorption technique with a time resolution that is intrinsically limited by the duration of the light decay, but practically by the repetition rate of the pulsed laser (typically 10–100 Hz). Fur-

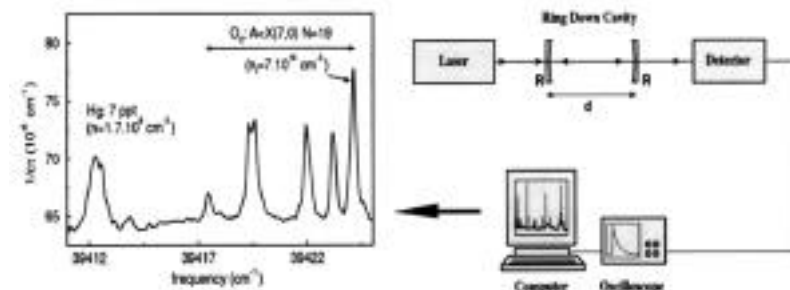


Figure 1 Experimental setup for CRD spectroscopy consists of a (pulsed) laser system; a ring down cavity formed by two highly reflective mirrors (reflectivity, R) placed at a distance, d ; a detector (e.g., a photomultiplier); a digital oscilloscope to record the decay transients; and a PC for the data processing. On the left is a CRD spectrum of laboratory air recorded around 253.7 nm (cavity length 45 cm, mirror reflectivity 99.7%). It demonstrates the capabilities of CRD spectroscopy; one can measure weak absorptions of abundant species (oxygen) and strong transitions of trace gas species (mercury).

of its initial value is called the ring down time, τ . In an empty cavity, the total loss is determined by the mirror reflectivity. This provides a measure for the zero-absorption baseline. An absorbing sample introduced into the cavity will increase the total cavity losses. As a result, the cavity ring down time will shorten:

$$\tau = \frac{d}{c[(1-R) + \kappa l]} \quad (1)$$

where d is the cavity length, c is the speed of light, R is the mirror reflectivity, and κ is the absorption coefficient of the absorber present over a pathlength, l , inside the cavity.

Suppose we have mirrors with a reflectivity of 99.99% placed at a distance of 0.5 m. The effective pathlength $d/(1-R)$ is then equal to 5000 m, and the decay time is

increased, the cavity ring down time will increase and can be determined more easily. In order to achieve high sensitivity in the absorption measurement, only a low accuracy in the time measurement is needed. For example, an accuracy for the determination of the ring down time of only 1% combined with a 10-cm-long cavity consisting of mirrors with a reflectivity of 99.999% leads to a minimum detectable absorption of 10^{-8} cm^{-1} . This high sensitivity is readily achieved with a rather simple experimental setup. A higher sensitivity requires more control over the coupling of the light into the cavity. Furthermore, special care should be taken in the data acquisition. A sensitivity of 10^{-10} cm^{-1} has already been demonstrated by Van Zee et al.²

and the ring down time can be determined. Using cw-CRD, higher repetition rates (kHz), a higher sensitivity ($10^{-10} - 10^{-12} \text{ cm}^{-1} \text{ Hz}^{-1/2}$) (see Spence et al.⁴), and a higher spectral resolution can be obtained than with pulsed CRD spectroscopy. Furthermore, in cw-CRD spectroscopy, high intracavity energies are achievable, resulting in higher light intensities impinging on the detector, improving the signal-to-noise ratios on the transients and therefore increasing the overall sensitivity. An additional advantage is that compact, easy-to-use, and inexpensive cw-diode lasers that have low power consumption and do not require cooling are available, which are interesting for trace gas detection applications at remote locations.

Applications

As a result of the high sensitivity, CRD spectroscopy can be used in fields in which strong absorptions of trace gas species or weak absorptions of abundant species need to be measured. Many research groups have used CRD successfully in their spectroscopic studies. The technique can easily be applied in different research fields in various experimental environments and has wide spectral coverage (UV-IR). CRD has also been used in supersonic jets, on molecules generated in discharges, in flow reactors, and in flames. The technique has been used for spectroscopic investigations of molecular species in order to obtain information on, for example, molecular structure, energy levels, and predissociation rates.

Additionally, CRD spectroscopy has been applied extensively in the field of trace gas analysis. Detailed studies of concentration profiles of radicals in flames have been carried out. The high temporal resolution of CRD has been used in the monitoring of species in chemical reactions. Furthermore, the combination of CRD spectroscopy with inductively coupled plasma (ICP) torches provides an experimental scheme that can monitor industrial waste processes and toxic emissions

In CEA spectroscopy, the measured time-integrated intensity is proportional to the ring down time of the cavity, and thus inversely proportional to the absorption coefficient.

16.67 μsec . An absorption of $\kappa = 10^{-8} \text{ cm}^{-1}$ over the full 50 cm will change the decay time to 16.58 μsec . An absorption spectrum can be obtained by measuring the empty cavity loss and the change in ring down time due to the absorber as a function of the wavelength of the laser. In practice, the empty cavity losses, since they mostly vary slowly with respect to the laser wavelength, can be determined from that part of the absorption spectrum wherein there are no losses due to the absorber. It is clear that the measurement of the absorption coefficient only involves the determination of two time constants. Furthermore, in a static cell experiment, $l = d$, and knowledge of the length of the cavity is not required for the determination of the absorption coefficient, κ .

The sensitivity attainable with CRD spectroscopy depends on the reflectivity of the cavity mirrors and the accuracy with which the ring down time can be determined. As the mirror reflectivity is

Since CRD involves measurements of the cavity decay time (typically in the nsec/ μsec range), this automatically sets the intrinsic limit for the achievable repetition rate of the measurements. In practice, using pulsed CRD spectroscopy, the duty cycle in absorption measurements is set by the maximum repetition rate of the pulsed light sources. To enhance the duty cycle, the use of cw-lasers is a perfect option.

The development and use of continuous wave-cavity ring down (cw-CRD) spectroscopy has become more widespread. In principle, cw-CRD is equivalent to pulsed CRD spectroscopy; again, the temporal behavior of the light exiting the cavity is studied. As soon as a sufficient amount of cw-light has been coupled into the cavity, the interaction between the cw-light and the cavity is broken down, preventing further entry of light into the cavity (see Romanini et al.³). Subsequently, the light inside the cavity will decay exponentially

in real time with a high sensitivity.⁵ Complete overviews of CRD research in the various experimental fields can be found in the review papers by Scherer et al.,⁶ Wheeler et al.,⁷ Cheskis,⁸ and Berden et al.⁹

The light source used in most CRD experiments is monochro-

from the difference between the cavity losses in the two directions. In this polarization-dependent-cavity ring down (PD-CRD) scheme, the rate of optical rotation is measured, which is placed directly on an absolute scale. By placing the cavity inside a magnetic field, the

compounds. They demonstrated a sensitivity to angle change of 4×10^{-8} rad cm⁻¹, which is substantially better than sensitivities for many commercial polarimeters employed in solution-phase studies.

Although most CRD experiments have been performed on gas phase species, there are a few studies on solids. If an optically transparent sample is placed inside the cavity in such a way that all resulting cavities are optically stable, reflections from the surface of the sample will remain in the ring down cavity, and thus will not be noticed as overall losses from the cavity. Of course, compared to the empty cavity, there will be additional losses due to, for example, absorption in the solid and reflections of the sample, which can no longer be captured in the ring down cavity. The authors have measured the polarization rotation as a result of the Faraday effect in a BK7 window using PD-CRD. Furthermore, they recorded the absorption spectrum of 20–30-nm-thick C₆₀ film deposited on a 3-mm-thick ZnSe substrate in the 8.5- μ m region (Figure 2).¹⁴

Pipino et al.¹⁵ successfully demonstrated the combination of

matic, but a polychromatic light source can be used as well in CRD spectroscopy. In 1996, Engeln and Meijer¹⁰ demonstrated this in so-called Fourier transform-cavity ring down (FT-CRD). The optical cavity was excited by a broad-band dye laser, and the light exiting the cavity was coupled into an FT-spectrometer. Ring down transients at each laser frequency were created by Fourier transforming the interferograms that were formed from the multiexponentially decaying transients measured at every interferometer arm-length difference. In this way, the absorption spectrum was constructed with a resolution determined by the FT spectrometer. Note that in FT-CRD spectroscopy, the decay rate of the light exiting the cavity is studied and thus is independent of light source fluctuations. Instead of an FT spectrometer, one can use a monochromator for dispersing the light exiting the cavity. One can scan the monochromator and measure the ring down transient at each wavelength, or use a time-resolved optical multichannel analyzer for recording the transients at many wavelengths simultaneously.¹¹

Even though the light used in CRD experiments is polarized, only a few schemes make use of this extra feature. Engeln et al.¹² placed the cavity between polarizers. The light exiting the cavity was split into two mutually orthogonal polarized components. The time dependence of both polarization directions was measured simultaneously. The information is obtained

plane of polarization can rotate due to dispersion (magnetic birefringence) or polarization-dependent absorption (magnetic dichroism). Since PD-CRD is only sensitive for para-magnetic species, it is possible to use it as a species-selective spectroscopic tool when measuring mixtures of various gases. The PD-CRD scheme can be modified in order to measure optical rotation in samples of chiral molecules in the gas phase. By inserting two quarter wave plates in the cavity, Vacarro and co-workers¹³ measured the optical rotation and differential absorption (circular dichroism) induced by the presence of chiral

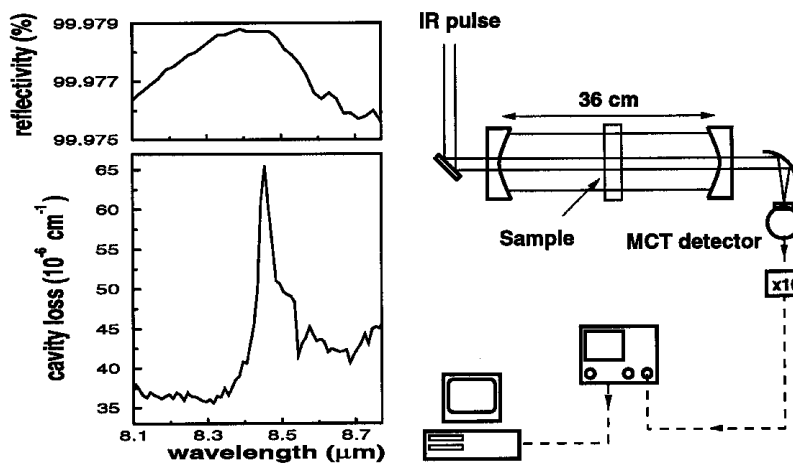


Figure 2 CRD spectroscopy on a solid sample of C₆₀. A thin film (20–30 nm) of C₆₀ is deposited on an optically flat ZnSe window. This window is placed inside the ring down cavity in such a way that the reflections from the surfaces are kept inside the cavity. The measured decay of the empty cavity is 5.6 μ sec, implying a reflectivity of 99.98% (upper panel). Inserting the window reduces the ring down time to 2.2 μ sec. Absorption of the thin film causes an additional loss. The recorded CRD spectrum (lower panel) shows a resonance at 8.45 μ m, which is one of the four IR active fundamental modes of C₆₀. MCT = mercury cadmium telluride.

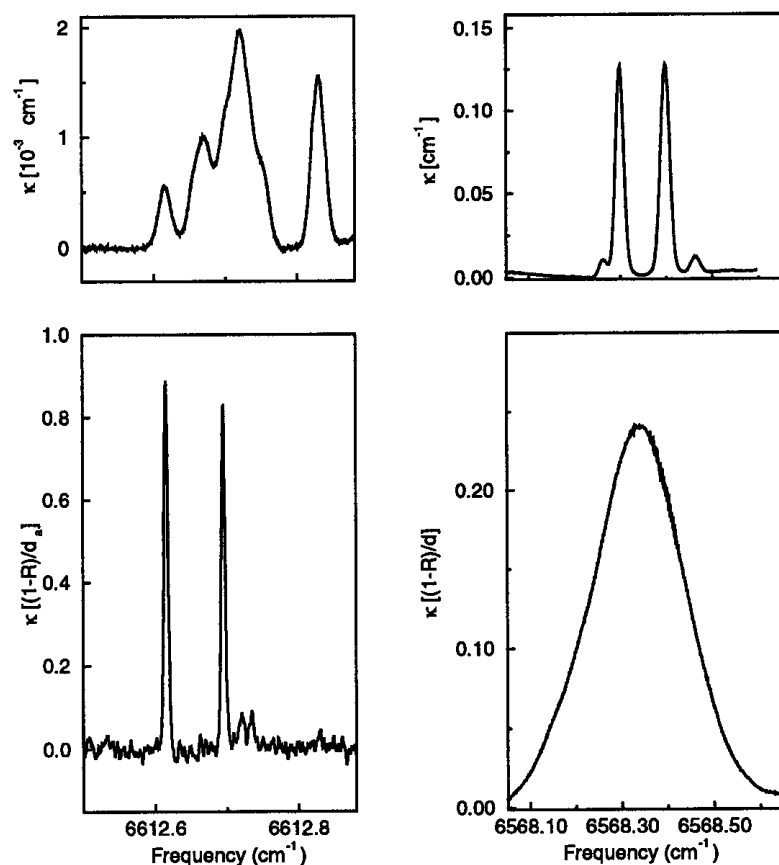


Figure 3 Ammonia has many rovibrational transitions in the 1.5- μm region that can easily be measured with a diode laser in a single-pass absorption cell (upper panels). Therefore, these transitions can be used for trace gas detection with CEA spectroscopy. The lower panel on the right shows the corresponding absorption spectrum of 1.2 ppm ammonia under atmospheric pressure. Furthermore, CEA spectroscopy can be used for high-resolution spectroscopy. This is shown in the lower panel on the left, where the CEA spectrum of jet-cooled ammonia (linewidth of 0.006 cm^{-1}) was measured. Comparing the upper and lower panel, it is evident that rotational and vibrational cooling results in a less congested spectrum. Jet-cooled spectra are very useful for understanding complex, room-temperature spectra.

attenuated total reflectance spectroscopy (which uses evanescent waves for probing optical absorptions) with CRD spectroscopy. Using this experimental scheme, they measured absorptions in a submonolayer of absorbed I_2 . By measuring the ring down times for two orthogonal polarization directions of the light, they showed that the I_2 molecules were preferentially oriented with their molecular axis parallel to the surface of the total internal reflection prism.

Cavity-Enhanced Absorption spectroscopy

Recently, the authors developed

an absorption technique that is an intermediate between direct absorption spectroscopy and CRD spectroscopy: Cavity Enhanced Absorption spectroscopy (CEA).¹⁶ This is a cw-absorption technique, and instead of the temporal behavior of the intensity inside the optical cavity, the total time-integrated intensity leaking out of the cavity is measured. It can be shown that the measured time-integrated intensity is proportional to the ring down time of the cavity, and thus inversely proportional to the absorption coefficient. A drawback is that CEA spectroscopy is not independent of the laser intensity, but since it is a cw technique, very sta-

ble light sources can be used. The CEA experimental setup approaches the experimental simplicity of the direct absorption technique, with the additional advantage of a sensitivity equal to CRD spectroscopy. Furthermore, CEA is a robust technique; therefore, an unstable environment (as encountered in, for example, in situ trace gas detection experiments) will not hinder the performance of the technique.

CEA spectroscopy has been used in normal cell experiments to measure the γ -band of oxygen and an overtone of ammonia at $1.5\text{ }\mu\text{m}$. O'Keefe et al.,¹⁷ using the same technique, measured absorption spectra of water vapor and carbon dioxide at $1.3\text{ }\mu\text{m}$. Figure 3 shows the CEA spectrum of ammonia recorded in a supersonic jet expansion.¹⁸ Furthermore, the sensitivity of CEA for trace gas detection under atmospheric conditions for ammonia (Figure 3) and water has been determined ($10^{-8}\text{ cm}^{-1}\text{ Hz}^{-1/2}$).¹⁹ Additionally, the CEA technique has been combined with magnetic rotation spectroscopy.¹⁶

Conclusion

Both CRD spectroscopy and CEA spectroscopy are highly sensitive and easy-to-use techniques that have found their way into a variety of experimental research fields. They have proven to be of great potential for spectroscopic purposes and, therefore, the application of these techniques in various experimental fields is expected to increase further. The potential for CRD, in particular, has been demonstrated in the number of papers that have appeared since its development.⁹ Even though CEA was developed only recently, it is already rapidly gaining interest in the spectroscopic and analytical research fields.

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